



## Short communication

## High-temperature passive direct methanol fuel cells operating with concentrated fuels

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## HIGHLIGHTS

- A high-temperature passive DMFC utilizing concentrated fuels was proposed.
- A H<sub>3</sub>PO<sub>4</sub>-doped PBI membrane was utilized as the electrolyte in this new passive DMFC.
- A peak power density of 37.2 mW cm<sup>−2</sup> was achieved at 180 °C with 16 M methanol.
- The effects of temperature and methanol concentration on performance were studied.
- The performance of this new DMFC was relatively stable during 132 h stability test.

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## ABSTRACT

Conventionally, passive direct methanol fuel cells (DMFC) are fed with diluted methanol solutions and can hardly be operated at elevated temperatures (>120 °C) because the ionic conductivity of Nafion-type proton exchange membranes depends strongly on water content. Such a system design would limit its energy density and power density in mobile applications. In this communication, a passive vapor feed DMFC capable of operating with concentrated fuels at high temperatures is reported. The passive DMFC proposed in this work consists of a fuel reservoir, a perforated silicone sheet, a vapor chamber, two current collectors and a membrane electrode assembly (MEA) based on a phosphoric acid doped polybenzimidazole (PBI) membrane. The experimental results reveal that the methanol crossover through a PBI membrane is substantially low when compared with the Nafion membranes and the PBI-based passive DMFC can yield a peak power density of 37.2 mW cm<sup>−2</sup> and 22.1 mW cm<sup>−2</sup> at 180 °C when 16 M methanol solutions and neat methanol are used respectively. In addition, the 132 h discharge test indicates that the performance of this new DMFC is quite stable and no obvious performance degradation is observed after activation, showing its promising applications in portable power sources.

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## 1. Introduction

Over the past decade, direct methanol fuel cells (DMFC) that can convert the chemical energy in the methanol to electricity without reforming, have attracted worldwide efforts of researchers due to their appealing features, including simple system design, ease in fuel handling and high energy density (4800 Wh L<sup>−1</sup>) [1–5]. Generally, DMFCs can be divided into two types: an active one that utilizes pumps and blowers (or compressors) to supply reactants and remove products, and a passive one that takes advantage of diffusion and natural convection to deliver fuel and oxidant [6]. As the passive DMFC consumes no additional power generated by the

fuel cell and consists of fewer auxiliary devices than does the active one, it is more suitable for powering the high-performance portable electronic devices such as smart phones, tablets and laptops.

Conventionally, Nafion<sup>®</sup> membranes from Dupont<sup>®</sup> are employed in passive DMFCs to conduct protons from the anode to cathode. Although the proton conductivities of Nafion membranes are good, these membranes are easily permeable to methanol and thus excess methanol in the anode will predominantly permeate through the membrane to the cathode, leading to fuel loss and a mixed potential at the cathode. To minimize the adverse effects of methanol crossover, diluted methanol solutions (<4 M) are usually fed to passive DMFCs directly. Such an operation, however, will significantly lower the energy density of a DMFC system [3,5], sacrificing the most attractive advantage of this type of fuel cell. To increase the energy density, a number of researches have been performed over the past few years, including modifying the

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existing Nafion membranes [7–9], developing new proton-conducting membranes [10–13], introducing novel fuel delivery schemes [14–19] and improving the water management [20–29].

In addition to the issue of methanol crossover, the use of Nafion membranes precludes a high-temperature operation ( $>120\text{ }^{\circ}\text{C}$ ) of the passive DMFC. This is because the proton conductivity of a Nafion membrane depends strongly on water; this membrane exhibits a fairly low proton conductivity at elevated temperatures due to the absence of liquid water. In fact, high temperatures can offer several desirable advantages [30–32]: 1) enhancement in the kinetics of electrochemical reactions at each electrode; 2) increase in the CO tolerance of catalysts; 3) improvement in the transport of fuel and oxidant to electrodes. Driven by such favorable features, operating DMFCs at high temperatures has received increasing attentions in recent years [33–41]. The high-temperature DMFC was first proposed by Wainright et al. [33] in the open literature. In their DMFC, a PtRu loading of  $4\text{ mg cm}^{-2}$  and a Pt loading of  $4\text{ mg cm}^{-2}$  were applied in the anode and cathode, respectively, and a phosphoric acid doped polybenzimidazole (PBI) membrane was used as a proton-conducting membrane for the first time; it was demonstrated that a peak power density of about  $120\text{ mW cm}^{-2}$  can be achieved with a water to methanol ratio of 4 (approximately 9 M) and pure oxygen at a temperature of  $200\text{ }^{\circ}\text{C}$ . Lobato et al. [36] investigated the effects of the operating temperatures, methanol concentrations and partial pressures on the performance of the high-temperature DMFC based on a  $\text{H}_3\text{PO}_4$ -doped PBI membrane with the help of a reference electrode. It was shown that a power density of  $138.5\text{ mW cm}^{-2}$  can still be obtained with a low catalyst loading of  $1\text{ mg cm}^{-2}$  at  $200\text{ }^{\circ}\text{C}$ . More recently, Mamlouk et al. [37] also studied the influence of operating conditions and found that the presence of phosphate in the anode electrode was a key factor leading to a poor performance. Rather than using  $\text{H}_3\text{PO}_4$ -doped PBI as electrolyte, Fan et al. [38] introduced a silicon carbide matrix to hold  $\text{H}_3\text{PO}_4$  and apply it to a high-temperature DMFC. A variety of operating and structural parameters including the stream pressure, cell temperature, design of the gas diffusion layer (GDL) and thickness of the silicon carbide were investigated experimentally in this new type of high-temperature DMFC.

Although promising, all the above-mentioned high-temperature DMFCs are based on the active supply of reactant and oxidant, which results in a complex system design and a parasitic power consumption. As a result, such DMFCs may not be suitable for the applications in portable devices. In addition, it has been known that for a passive DMFC operated with neat methanol, due to water starvation, its optimal operating temperature is rather low, typically lower than  $50\text{ }^{\circ}\text{C}$  [42], when a Nafion membrane is used as a polymer electrolyte. Obviously, such a low operating temperature would limit its improvement in performance. In this work, to simultaneously increase the energy density and the operating temperature, a passive vapor feed DMFC capable of operating with concentrated fuels at high temperatures was designed and tested. Particular focus was paid to its performance characteristic and the feasibility of a  $\text{H}_3\text{PO}_4$ -doped PBI membrane under passive operation.

## 2. Experimental

### 2.1. Preparation of membrane electrode assemblies (MEA)

A  $40\text{ }\mu\text{m}$ -thick PBI membrane was used as a polymer electrolyte in this work. To make the PBI membrane conduct protons, it was immersed in a 75 wt.%  $\text{H}_3\text{PO}_4$  solution (Acros Organic) at a temperature of  $80\text{ }^{\circ}\text{C}$  for at least 24 h until a doping level of approximately 6 was achieved. Toray<sup>®</sup> 090 carbon papers with the thickness of  $280\text{ }\mu\text{m}$  and 10 wt.% polytetrafluoroethylene (PTFE) content were used as backing layers for both anode and cathode electrodes. To reduce the contact resistance and the loss of catalysts, a microporous

layer (MPL) made of Vulcan<sup>®</sup> XC-72 carbon black and PTFE was brushed onto one side of the backing layer; the carbon loading and PTFE content in the MPL were  $2\text{ mg cm}^{-2}$  and 15 wt.%, respectively. Commercially available catalysts from Johnson Matthey<sup>®</sup>, Hispec<sup>®</sup> 10000 PtRu/C and Hispec<sup>®</sup> 9100 Pt/C, were employed respectively in the anode and cathode with the same loading of  $2\text{ mg cm}^{-2}$ . The catalyst binder used in this work was PTFE, the content of which was 10 wt.% for both electrodes. To increase the triple phase boundaries in the catalyst layers, both electrodes were loaded with  $10\text{ mg cm}^{-2}$   $\text{H}_3\text{PO}_4$  by pipetting 5 M  $\text{H}_3\text{PO}_4$  solutions onto the surface of the catalyst layer. The active area of the electrode was  $2.0 \times 2.0\text{ cm}^2$  and the MEA was tested without hot pressing.

### 2.2. Single cell design of a passive vapor feed DMFC

Fig. 1 shows the single cell fixture of the passive vapor feed DMFC used in this work. This single cell was composed of a cathode end plate, a cathode current collector, a MEA based on a  $\text{H}_3\text{PO}_4$ -doped PBI membrane, an anode current collector, a methanol vapor chamber with a built-in  $\text{CO}_2$  venting hole, a perforated silicone sheet, a fuel reservoir with a volume of 13.8 mL and an anode end plate, all of which were clamped together with 8 bolts. In order to control the operating temperature, the cathode end plate was built in with two holes for electrical heating rods and one hole for temperature sensing. It should be mentioned that the electrical heating was added to mimic the high-temperature operation and it may be unnecessary in a practical passive DMFC as a high temperature can be attained by proper thermal insulation. Both the anode and cathode current collectors were made of 316L stainless steel and were perforated to form 36 holes with the diameter of 2.6 mm, which resulted in an open ratio of 47.8%. The 10 mm thick silicone sheet was also drilled to gain an open ratio of 15.7% and was employed to control the delivery of methanol vapor.

### 2.3. Electrochemical instrumentation and test conditions

An Arbin<sup>®</sup> BT-5HC multiple channel test station was applied as an external electrical load and to record the performance results of

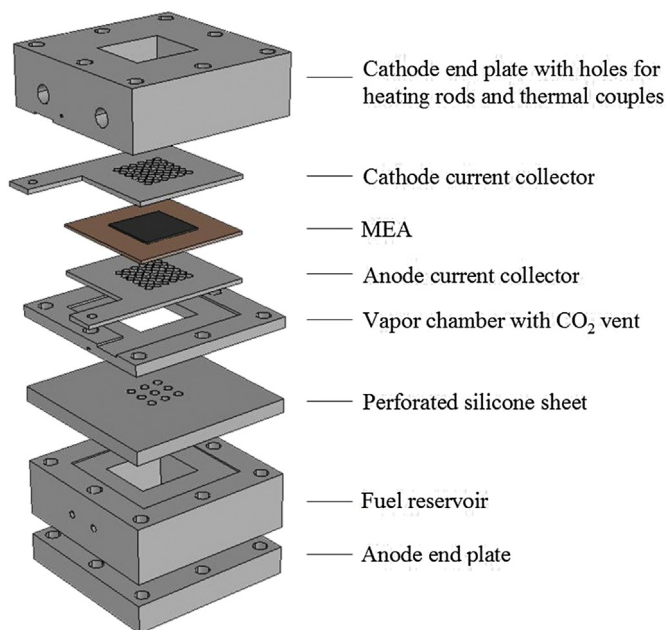


Fig. 1. Single cell design of a passive vapor feed DMFC based on a  $\text{H}_3\text{PO}_4$ -doped PBI membrane.

the passive vapor feed DMFC under various operating conditions. To attain the polarization curves, the passive DMFC was first kept at open circuit condition (OCC) for 30 min to ensure a stable operation of the fuel cell, followed by the discharges at a series of predefined currents. The test was repeated until reproducible performance was achieved. The ambient temperature and the relative humidity for all the measurements were about 24–26 °C and 80–90 %, respectively. In order to investigate the operating stability of the high-temperature DMFC, a 132 h short-term stability test was conducted in this work. For the convenience of fuel injection, the anode fuel reservoir of the fuel cell was connected to a syringe pump (Cole-Parmer® EW-74905-12) with a flow rate of 0.015 mL min<sup>-1</sup> and the syringe was refueled every 11 h. During refueling, the fuel cell was kept at OCC for no more than 5 min. The operating temperature, feeding methanol concentration and discharge current density for the stability test were 180 °C, 16 M and 50 mA cm<sup>-2</sup>, respectively.

#### 2.4. Measurement of methanol crossover current density

The methanol crossover was measured by voltammetric method originally proposed by Ren et al. [2]. To carry out this measurement, the cathode of the passive DMFC was actively supplied with nitrogen (humidified at 80 °C) at a flow rate of 500 sccm to generate an inert environment and to provide sufficient water for the methanol oxidation reaction (MOR) on the cathode. During the measurement, the cell was charged at a voltage of 0.85 V to facilitate the oxidation of permeated methanol from the anode and the charge current, known as limiting methanol crossover current [2], was recorded until the current was stable. It should be mentioned that the actual methanol crossover current should be higher than this limiting crossover current as methanol in the cathode would be dragged to the anode by electro-osmosis [2]. However, due to substantially small electro-osmotic drag coefficient of a PBI membrane [34] and rather low current across the cell, the methanol dragged by electro-osmosis is negligible and the measured limiting crossover current can be viewed approximately as the actual methanol crossover current.

### 3. Results and discussion

#### 3.1. Effect of operating temperatures

In order to investigate the performance characteristics of a passive vapor feed DMFC at elevated temperatures, the cell temperature is controlled to be increased from 120 to 200 °C with feeding neat methanol to the anode; the experimental results are shown in Fig. 2. It is interesting to see that the peak power densities of the PBI-based passive DMFC fed with neat methanol are 22.1 mW cm<sup>-2</sup> and 25.3 mW cm<sup>-2</sup>, respectively, at the temperatures of 180 °C and 200 °C. Such power densities are comparable to those of Nafion-based passive DMFC operated at low temperatures; according to the literature [15–29], the peak power densities of passive DMFCs fed with neat methanol are in the range of about 20–30 mW cm<sup>-2</sup>. These preliminary results of a PBI-based passive DMFC seem encouraging and promising as the MEAs and operating conditions employed here are without optimization. In addition, it is seen in Fig. 2 that the cell performance increases significantly with the temperature. For instance, the open circuit voltage (OCV) and peak power density increase, respectively, from 0.503 to 0.632 V and 3.8 to 25.3 mW cm<sup>-2</sup> when the temperature is elevated from 120 to 200 °C. Such an improvement can be attributed to the acceleration in the kinetics of MOR in the anode and oxygen reduction reactions (ORR) in the cathode, the enhancement in CO tolerance of catalysts and the increase in the proton conductivity of H<sub>3</sub>PO<sub>4</sub> [35] as well as the reduction in mass transport losses of

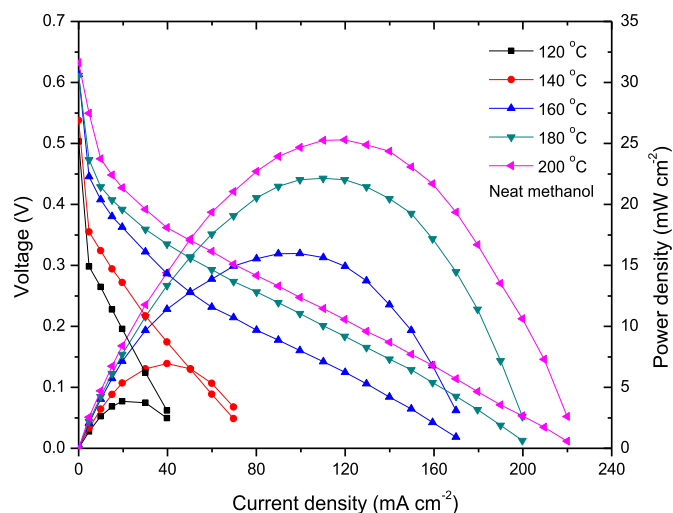


Fig. 2. Effect of operating temperatures on the performance of the passive vapor feed DMFC fed with neat methanol.

methanol vapor and oxygen. Meanwhile, it can be found in Fig. 2 that the performance gain is large with an increase in the temperature from 140 to 160 °C; the peak power density increases from 6.9 to 16.0 mW cm<sup>-2</sup>, representing an increase by a factor of 2.3. On the contrary, further increasing the temperature from 180 to 200 °C results in a much smaller increase in the peak power density, only 3.2 mW cm<sup>-2</sup>. This might be because the favorable effects of increasing temperature are counteracted by increased methanol crossover, larger evaporative losses of water [42] and H<sub>3</sub>PO<sub>4</sub> from electrodes, and dehydration of H<sub>3</sub>PO<sub>4</sub> to form less conductive pyrophosphoric acid [43]. This phenomenon suggests that to attain a reasonable performance, the practical operating temperature for a DMFC based on H<sub>3</sub>PO<sub>4</sub>-doped PBI membrane should be within the range of 160–200 °C.

#### 3.2. Effect of methanol concentrations

The effect of methanol concentrations is investigated in this work by feeding the passive DMFC with various concentrations from 8 to 24.7 M (neat) and the operating temperature is controlled

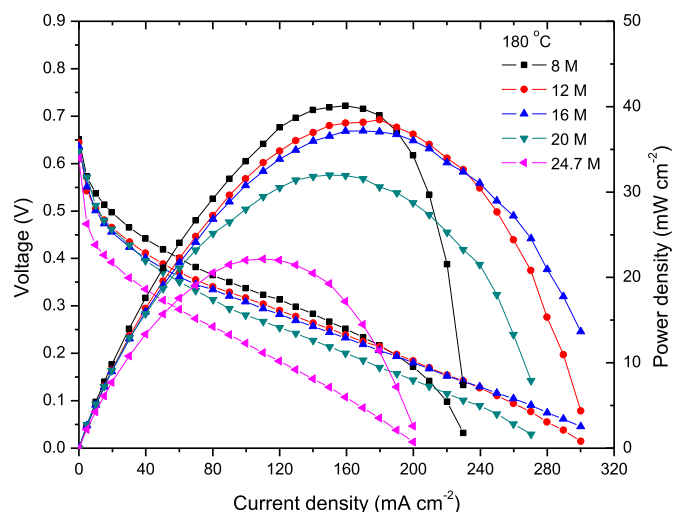


Fig. 3. Effect of methanol concentrations on the performance of the passive vapor feed DMFC at 180 °C.

at 180 °C; the performance results are shown in Fig. 3. It can be seen that all the OCVs are higher than 0.6 V even feeding concentrated methanol directly; the OCVs are 0.651 V, 0.644 V, 0.635 V, 0.626 V and 0.611 V, respectively, for the concentrations of 8 M, 12 M, 16 M, 20 M, 24.7 M. These high OCVs with concentrated methanol suggest that compared with conventional Nafion membranes, the methanol crossover through a PBI membrane should be significantly small. To prove such hypothesis, limiting methanol crossover current densities (approximately equal to the actual methanol crossover current densities at OCC) at a variety of methanol concentrations and operating temperatures are measured and presented in Fig. 4. It can be seen in Fig. 4 that the limiting methanol crossover current density increases with methanol concentrations and temperatures, respectively, showing a similar trend to that of Nafion membranes [2]. However, the crossover current density with a PBI membrane is substantially lower than that with a Nafion membrane; as shown in Fig. 4, the limiting crossover current density with a PBI membrane at 200 °C and neat methanol (24.7 M) is only 35.425 mA cm<sup>-2</sup> while it is as high as 193.6 mA cm<sup>2</sup> at 130 °C and 1 M methanol for a Nafion 117 membrane [2]. Hence, the PBI membrane is a good candidate for DMFC operated with highly concentrated fuels [34,36]. In addition, it can be seen in Fig. 3 that the cell performance generally increases with a decrease in the methanol concentration especially at the low current density region (<200 mA cm<sup>-2</sup>); the peak power densities shown in Fig. 3 are 22.1 mW cm<sup>-2</sup>, 32.0 mW cm<sup>-2</sup>, 37.2 mW cm<sup>-2</sup>, 38.5 mW cm<sup>-2</sup> and 40.1 mW cm<sup>-2</sup>, respectively, at the concentrations of 24.7 M, 20 M, 16 M, 12 M and 8 M. The reasons leading to an improved performance with a reduction in the methanol concentration can be explained as follows. Firstly, a lower methanol concentration means a higher water humidity in the electrodes. High humidity can facilitate the hydration of the H<sub>3</sub>PO<sub>4</sub> in the catalyst layers and the PBI membrane, which increases its proton conductivity [35]. As a result, more triple phase boundaries in the catalyst layers and proton transfer pathways in the PBI membrane are formed, thereby lowering the kinetic and ohmic losses of the DMFC. Secondly, it has been known that the MOR in the anode needs to consume water to form CO<sub>2</sub> and the MOR will become incomplete when the molar ratio of methanol to water is larger than about 1 [20,36,44], corresponding approximately to 17 M. The incomplete MOR will result

in a significant production of by-products such as methylformate and methylal, and lead to an increase in the anode overpotential. This explanation is in good agreement with experimental results; as shown in Fig. 3, the variation in the performance with the concentrations of 8–16 M (all the ratios of methanol to water are lower than 1) is small and their performances are much higher than those with 20 M (methanol/water = 1.9) and 24.7 M (methanol/water = ∞). Thirdly, as shown in Fig. 4, the reduction in the methanol concentration leads to a decrease in methanol crossover current density and thus increases the cathode performance. However, it is worth mentioning that the effect of methanol crossover on the performance should be minor because feeding anode with various methanol concentrations from 8 to 24.7 M results in only a small variation in the OCVs and all the measured limiting crossover current densities are rather low, as shown in Figs. 3 and 4. Furthermore, it is found in Fig. 3 that at the high current density region (>200 mA cm<sup>-2</sup>), the performance and the maximum current density of the DMFC fed with 16 M methanol solutions are higher than those with 8 M and 12 M. This is because the high current density region is dominated by concentration polarization and a higher methanol concentration can better satisfy the demand of methanol for MOR. Hence, it can be seen in Fig. 3 that when the methanol concentration is higher than 8 M, no limiting current is observed; the supply of methanol become insufficient when feeding 8 M methanol solutions to the anode and the limiting current density at 8 M is found to be about 230 mA cm<sup>-2</sup> with the present fuel cell structure. From the above experimental results, 16 M seems to be an optimal methanol concentration for the present passive vapor feed DMFC in terms of the performance and energy density.

### 3.3. Short-term stability test

To study the operating stability of a PBI-based DMFC fed with concentrated fuel, a 132 h discharge test is performed at a current density of 50 mA cm<sup>-2</sup>, a temperature of 180 °C and a methanol concentration of 16 M; the experimental results are shown in Fig. 5. The dash lines in Fig. 5 indicate the time for refueling the syringe pump at every 11 h. It is clear to see that the average cell voltage increases gradually during the first 44 h of the test, exhibiting a similar activation behavior to that of the high-temperature proton exchange membrane fuel cell (HT-PEMFC) [45–47]. The increase in the performance during activation period should be associated

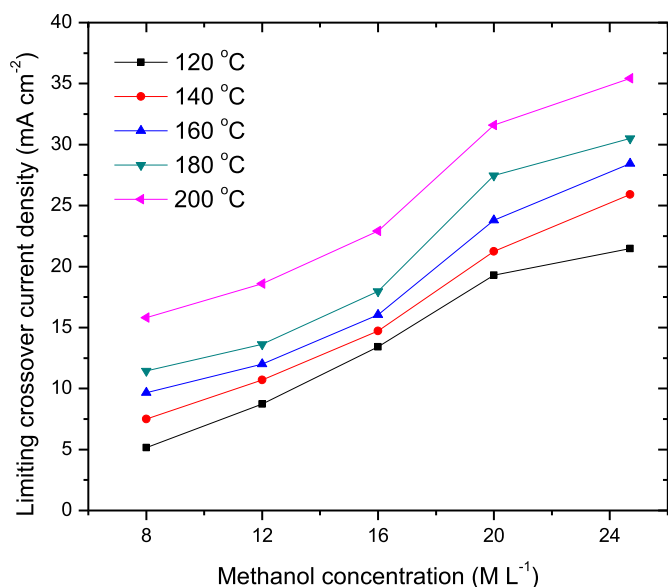


Fig. 4. Limiting methanol crossover current densities at a variety of methanol concentrations and temperatures.

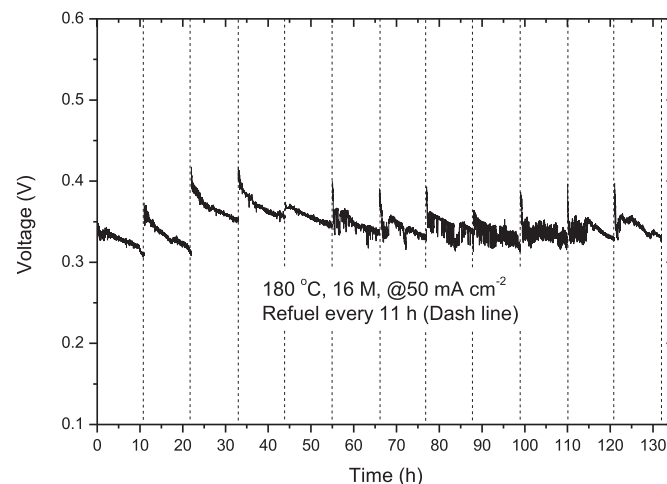


Fig. 5. Short-term stability test of a vapor feed DMFC with 16 M methanol solutions (cell temperature: 180 °C; discharge current density: 50 mA cm<sup>-2</sup>).



with the hydration and/or redistribution of  $\text{H}_3\text{PO}_4$  in the membrane and the catalyst layers, thereby decreasing the ionic resistance and extending the triple phase boundaries. After 44 h, although voltage fluctuation happens occasionally, the average cell voltage becomes relatively stable (about 0.34 V) and no obvious or permanent performance degradation is observed in the following 88 h test. The result of this preliminary stability test is rather encouraging and indicates that this new type of DMFC is capable of running with concentrated fuels stably at high temperatures and may be a good candidate for portable power sources, though the duration of the test is short when compared with that of a HT-PEMFC. Future works on a much longer durability test is of great importance to gain deeper understanding of the long-term operating characteristics.

#### 4. Concluding remarks

The use of a conventional proton-conducting membrane, namely Nafion, would limit the improvement in both the energy density and power density of a passive DMFC due to its high methanol permeability and significantly low ionic conductivity at elevated temperatures. Motivated by a quest for an improved system design, this work presents a new type of passive DMFCs that can be operated with concentrated fuels at high temperatures. The preliminary results show that the passive vapor feed DMFC can yield a peak power density of  $22.1 \text{ mW cm}^{-2}$  at an operating temperature of  $180^\circ\text{C}$  even when neat methanol is fed directly. Such a performance is already comparable to those based on Nafion membranes at low temperatures and its potential is far less than fully unlocked. Future improvement in PBI-based passive DMFCs may include developing highly-conductive proton-conducting membranes to reduce ionic resistance, modifying the electrode designs to retain phosphoric acid, improving the impregnation of phosphoric acid into electrodes to maximize triple phase boundaries.

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